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(54) Title of the Invention: Method to Produce Surface Modified Alumina Ceramics

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Description

1. Title of the Invention : Method to Produce Surface Modified Alumina Ceramics

2. Scope of the Patent Application

(1) Method to produce surface modified alumina ceramics characterized by the fact that after the material which includes silicon dioxide is coated on the alumina formed body or on the surface of an alumina ceramic, it is baked, and that the glass component that remains on the surface of the said ceramic that is obtained is eluted out, and in this way, the needle- like mullite is formed on the surface of the alumina ceramic.

(2) Method to produce surface modified alumina ceramics characterized by the fact that the silicon - dioxide- containing- material is at least one material selected from the group of : clay minerals of which the main components are aluminum oxide and silicon dioxide, the mixture of aluminum oxide powder or aluminum hydroxide powder and silicon dioxide powder or silicate glass powder, or a water based slurry of these, as was described in Claim 1.

3. Detailed Explanation of the Invention

[Field of Utilization in Industry]

This invention relates to the method to produce surface modified alumina ceramics, and in particular, it relates to the improvement in the ability to adhere with the metal that is required for the semiconductor integrated circuit substrate or the engineering ceramics by increasing the specific surface area of the surface, or relates to obtaining the new catalyst supports.

[Existing Technology]

Alumina ceramics have excellent mechanical strength, excellent heat characteristics, and excellent electric characteristics, etc., so that they have been used widely in various industrial fields. Especially, the demand for these has increased for use as the

substrates for the semiconductor integrated circuits, and in order to form the electrodes for connections or electrical circuits on the substrate, the desired conductive material such as metal, etc., is printed or adhered on the alumina ceramic, and thereafter it is baked. However, when the surface of the alumina ceramic is smooth, the metal, etc., that is formed on the surface tends to be peeled off easily, so that in order to improve the tight adhering ability between the alumina ceramic and the metal, etc., the surface of the alumina ceramic is made rough by mechanical methods such as sand blasting, etc., or by chemical etching in which the grain boundaries are eluted out by an acid such as hydrogen fluoride, phosphoric acid, or by an alkali such as sodium hydroxide, etc.

[Problem That this Invention Intends to Solve]

When the surface of an alumina ceramic is made by rough by mechanical methods or by chemical methods, the roughness of the surface structure is non-uniform, and it is difficult to obtain the fine grooves or protrusions, therefore, not only the adhering ability with the metal, etc., easily decreases, but also it used to take a long time to roughen the surface.

[Method to Solve the Problem]

In order to make the surface structure of the alumina ceramics to be evenly rough, and to increase the specific surface area and to improve the attachment with the metals, etc., that are formed on the surface, the inventors of this invention paid attention to the fact that the objective can be achieved by forming the layer which is extremely strong and which has a large specific surface area also, instead of removing a part of the surface by mechanical or chemical methods as in the existing case. So they investigated the layers that are going to be formed on the alumina ceramics. As the result, they discovered that the layer with a large specific surface area and with high attaching ability, can be obtained when the crystals of mullite, which includes alumina that is the main component of the alumina ceramics, and of which the sintering

temperature of alumina and the temperature for growing the needle - like crystals are almost the same, is grown densely in three dimensions.

Namely, at least one material selected from the group of : clay minerals of which the main components are aluminum oxide and silicon dioxide, the mixture of aluminum oxide powder or aluminum hydroxide powder and silicon dioxide powder or silicate glass powder, or a water based slurry of these, is coated on the alumina formed body or on the surface of the alumina ceramic, and thereafter it is baked at 1200 to 1700 °C, and the glass component that remains on the surface of the alumina ceramic that is obtained is eluted out, and by this, the needle- like mullite is formed on the surface of the alumina ceramics.

Here, the alumina formed body of this invention includes not only the formed body that is comprised of only alumina as the ceramic component, but also the formed body of which the main component is alumina that also includes silica, magnesia, etc., in addition to alumina. Similarly, the meaning of alumina ceramics includes not only the ceramics made out of only alumina, but also the ceramics which include silica and magnesia as well as the alumina which is the main component. Also, this invention can be applied to both the un-sintered alumina formed bodies, and the sintered alumina ceramics.

Next, the case of using the un-sintered alumina formed body will be explained.

The alumina that can be used here is the powder of which the grain diameter is 0.1 to 10 μm and which practically does not contain other components, for example, alumina powder with an average grain diameter of 0.5 μm (α- type alumina, commercial name ABS-12, a product of Sumitomo Chemical Co. This contains Fe_2O_3 : 0.01, SiO_2 : 0.02, Na_2O : 0.03 as impurities. units are all wt %.), alumina powder with an average grain diameter of 5 μm (α- type alumina, commercial name AM-25, a product of

Sumitomo Chemical Co. This contains Fe_2O_3 : 0.01, SiO_2 : 0.02, Na_2O : 0.03 as impurities, units are all wt %.), and alumina powder with an average grain diameter of 10 μm (α- type alumina, commercial name AM-28, a product of Sumitomo Chemical Co. This contains Fe_2O_3 : 0.01, SiO_2 : 0.02, Na_2O : 0.27 as impurities, units are all wt %.). Using these powders, methyl cellulose, poly vinyl alcohol, wax, a thermosetting resin, a thermoplastic resin, etc., are added at 2 to 30 wt % as a binder, and it can be formed into pellets, honey comb or thin plates by extrusion forming, cast forming, etc., and then, it is sufficiently dried, and thus, the alumina formed body can be obtained.

Next, the material which forms mullite is coated on the surface of the formed body or the formed body is submerged, and the mullite forming material is attached to the surface. The clay minerals such as kaolin or pottery clay for the pottery and ceramics can be listed as the mullite forming materials, and in addition, cristobalite powder, tridymite powder, plate glass powder, colloidal silica or a silicate glass such as water glass, or the powder mixture of aluminum oxide powder or aluminum hydroxide powder and silicon dioxide powder, can be used also. In the case when the powder mixture of silicon dioxide and aluminum hydroxide or aluminum oxide, etc., is used as the raw material, it should be selected in the particle size range of 0.1 to 100 μm, however, in the case of aluminum oxide or aluminum hydroxide, 0.1 to 10 μm particles are preferred, and in the case of silicon dioxide, 0.5 to 50 μm particles are preferred.

In the case of using the powder of silicate glass, or a mixed powder of silicon dioxide and aluminum oxide or aluminum hydroxide, it can be used as the powder as it is, or it can be used as a slurry in which 1 ~ 10 parts of the raw material powder of is dispersed in 99 ~ 90 parts of water as the weight ratio.

The alumina formed body or alumina ceramics on which the mullite forming material was attached, is then baked at 1200 to 1700 °C for 0.1 to 10 hours, preferably 1 to 3 hours, and thereafter, the glass component or the glass phase that remains in the

baked body should be eluted out with an acid or an alkali. In the case when hydro fluoric acid is used as the acid, it should be submerged in the acid with a concentration of 2 to 20 % for 10 minutes to 3 hours at a temperature of 20 to 50 °C. In the case when an alkali such as sodium hydroxide or potassium hydroxide is used, it should be submerged in an autoclave at a temperature of 100 to 200 °C for 30 minutes to 10 hours using the alkali at a concentration of 0.1 N to 2 N. After this elution treatment, the post treatment should be done such as water washing, etc., by normal methods.

Using a method like this, the fine needle- like mullite grows three dimensionally, attaching to the surface of the alumina ceramic, and the surface modified alumina ceramic in which the needle- like crystals are densely grown in a crossing pattern, can be obtained. The obtained needle- like mullite shows the morphology of whisker- like crystals of which the longer diameter is normally 1 ~ 30 μm, and the shorter diameter is 0.1 to 2 μm, and which are thermally stable to about 1750 °C, and which are difficult to be deformed.

The surface modified alumina ceramics obtained are porous materials in which pores of 0.1 to 1 μm pore diameter are formed, and the porosity is proportional to the thickness of the needle- like mullite layer, and it can be adjusted to be in the range of 5 to 40 %. In addition, the needle- like mullite is strongly attached to the foundation of the alumina ceramic, therefore, even if it is heated to 400 to 500 °C and then quickly cooled, it does not peel off easily.

Thus, the case of using an alumina formed body was explained. However, instead of using an alumina formed body, a glass which is difficult to be melt - deformed at 1200 to 1400 °C, for example quartz glass, can be used too. In that case, an alkali component such as sodium oxide, potassium oxide, etc., is added at several % into the alumina powder or aluminum hydroxide powder, and it is kneaded, and this material is

coated on the surface, and after it is baked, it is treated with hydro fluoric acid, and in this way, the needle- like mullite can be grown densely on the surface of quartz glass.

[Effect]

By the method of this invention, the roughness of the surface structure of the alumina ceramics can be made uniform easily and efficiently, and at the same time, the specific surface area can be increased, so that it can increase the attachability of metal, etc., the adsorbability of ions, etc., and the penetrating ability of solder, etc.

Next, this invention will be explained in more detail referring to actual examples.

[Example 1]

Methyl cellulose was added as the binder at 10 wt % into alumina powder with an average grain diameter of 0.5 μm (α- type alumina, commercial name AHS-12, a product of Sumitomo Chemical Co. This contains Fe_2O_3 : 0.01, SiO_2 : 0.02, Na_2O : 0.03 as impurities, units are all wt %.), and after it was kneaded, it was extrusion formed into a thin plate. The obtained formed body was sufficiently dried, and a formed body of alumina, weighing 50g (thickness of 2 mm, width of 50 mm, and a length of 160 mm) was obtained.

10 weight parts of clay mineral powder of which the average grain diameter was 1 μm, and 90 weight parts of water were mixed, and a slurry in which the mullite forming material was dispersed, was prepared. The said alumina formed body was submerged in 100 mL of this slurry and it was impregnated. Thereafter, the alumina formed body was baked at 1650 °C for 2 hours. The glass component or the glass phase that remained in the alumina ceramic that was obtained, was eluted out with 4.6 % - hydro fluoric acid for 1 hour, and then it was washed with water, and thus the surface modified alumina ceramic in which the needle- like mullite grew densely on the surface, was

obtained.

Figure 1 shows an electron micrograph of the needle- like mullite crystals that grew densely on the surface of the obtained surface modified alumina ceramic at 3500 X magnification. Figure 2 shows an electron micrograph of the cross sectional structure of the said ceramic at 1500 X magnification.

The thin plate- like surface modified alumina ceramic was submerged in a ferric nitrate solution of which the concentration was 0.1 mole / L for 2 hours, and it was impregnated, and thereafter the iron supported in the said ceramic was eluted out with hydro chloric acid, and it was analyzed by absorption. As the result, the supported iron was 2.7 mg per 1 g of the said ceramic.

Also, nickel was deposited for 10 minutes by the vacuum vapor deposition method, and thereafter, the nickel was eluted out with 1N- hydrochloric acid. According to the absorptiometric analysis, 34 mg of nickel was attached.

Melted solder was applied on the said ceramic on which the nickel was vapor deposited to check the wetability. The solder penetrated well.

Concerning the mechanical strength, a thin plate of the said ceramic with a width of 10 mm, a length of 50 mm and a depth of 1mm, was adhered by cyano acrylate type resin, and the flexural strength was checked, and it was found to be 20.5 kg / mm^2.

[Example 2]

Pellets, of which the grain diameter was 0.5 to 1 (mm? *illegible*), of surface modified alumina ceramic were produced by the same method as in Example 1, and after it was submerged in a ferric nitrate solution of which the concentration was 0.1 mole / L for 2

hours, the iron supported in the said ceramics was eluted out with hydro chloric acid. According to the absorptiometric analysis, the supported iron was 6.5 mg per 1 g of the said ceramic.

[Example 3]

A 0.2 (mm? *illegible*) thick honey comb- like alumina ceramic for the catalyst support was produced by the same method as in Example 1, and after it was submerged in a ferric nitrate solution of which the concentration was 0.1 mole / L for 2 hours, the iron supported in the said ceramic was eluted out with hydro chloric acid. According to the absorptiometric analysis, the supported iron was 3.5 mg per 1 g of the said ceramic.

[Comparison]

The amount of metal supported in the alumina ceramic of which the surface was not modified with needle- like crystals of mullite, was measured by the same method as in Examples 1, 2 and 3. This amount was 0.8 mg, 2.2 mg and 1.2 mg per 1 g of alumina ceramic for the cases of the thin plate, pellets and the honey comb- like catalyst support, respectively.

Also, the thin plate- like alumina ceramic of which the surface was not modified, was checked for its flexural strength by the same method as in Example 1, and this was found to be 11.4 kg / mm^2.

[Effect of the Invention]

As was explained above, according to this invention, the roughness of the surface structure of the alumina ceramics can be made uniform, and the specific surface area can be increased, so that the surface modified alumina ceramics in which the metal attachability, the ion adsorption, and the penetration of solder, etc., were improved, can be produced easily.

4. Simple Explanation of Figures

Figure 1 is the electron micrograph, instead of a drawing, which explains the structure of the needle- like mullite crystals that grew densely on the surface of the obtained surface modified alumina ceramics of this invention.

Figure 2 is an electron micrograph instead of a drawing which explains the structure of the cross section of the alumina ceramic indicated in Figure 1.

Figure 3 is the electron micrograph, instead of a drawing, which explains the crystal structure of the surface of the non- modified alumina ceramics.

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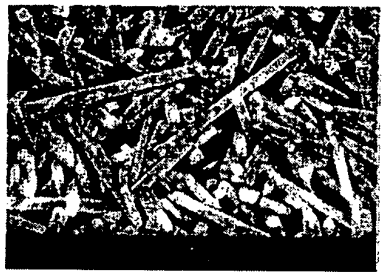
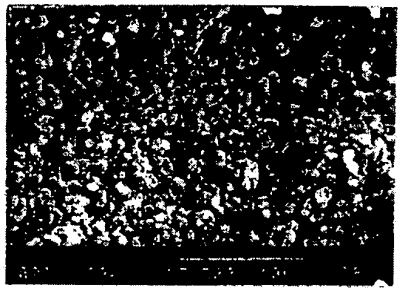


Figure 1

Figure 2

Figure 3



(Please see the original figures for better quality photos. Figure 3 is on p. 430, and Figures 1 and 2 are on p. 431, Translator)